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PHASE COMPOSITION OF GLASS CERAMICS OF THE SYSTEM $K_2O - Li_2O - Al_2O_3 - SiO_2 - SnO_2 - ZrO_2$ FOR METAL-CERAMIC COATINGS

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The sequence of formation of crystalline phases (cassiterite, lithium metasilicate, leucite and baddeleyite) is determined and the solubility of SnO_2 and ZrO_2 in the system $K_2O - Li_2O - Al_2O_3 - SiO_2 - SnO_2 - ZrO_2$ is studied. Glass ceramic based on the indicated system gives a level of the physical-mechanical and chemical properties which are necessary for obtaining the opaque layer of dentures.

Key words: glass ceramic, crystalline phases, formation of phases, coatings, properties.

The laws of separating leucite $K_2O \cdot Al_2O_3 \cdot 4SiO_2$, as the main crystalline phase in formation of a glass crystalline coating in metal-ceramic dentures, during heat-treatment of glass in the system $K_2O - Li_2O - Al_2O_3 - SiO_2$ are examined in [1, 2]. It is leucite that makes it possible to obtain high values of CLTE ($14 \times 10^{-6} - 15 \times 10^{-6} K^{-1}$) in glass ceramic, which are required for strong seals of glass ceramic materials (GCM) to nickel-chromium alloys. At the same time it turned out to be impossible obtain other required properties of glass ceramic — opacity, low chemical solubility and high strength — without additional adjustment of the compositions of tin and zirconium oxides.

The main purpose of tin oxide is to increase the degree of opacification of the so-called opaque layer of the glass ceramic coating, masking the color of the metal substrate. It is known that SnO_2 has found wide application in glass as an opacifier [3] and is considered to be one of the best opacifiers for glasses and enamels. The opacification is due to the fact that the solubility of SnO_2 in silicate melt is limited; above this level tin dioxide precipitates from the melt in the form of finely disperse crystals of cassiterite. The solubility of SnO_2 in melts with cordierite and spodumene compositions is 5–7%,² greatly exceeding the chemical stability and strength characteristics of glass [4, 5]. In this case CnO_2 enters the anionic part of the structure of glass in the form of the groups $[SnO_4]$ and strengthens the structure. Above the solubility limit and under oxidizing conditions $[SnO_6]$ groups, comprising the cationic part of the structure and playing the role of a modifier, are easily formed [6, 7].

The property of limited solubility of SnO_2 in silicate melt has found application in the technology of vitals, where tin dioxide in amounts 10–11% is a catalyst for crystallization [7]. All this confirms the desirability of adding SnO_2 into the glass under study both from the standpoint of increasing the properties of the glassy component and as a strong opacifier and catalyst of crystallization, forming an independent crystal phase — cassiterite.

Synthesis of glasses in the system $K_2O - Li_2O - Al_2O_3 - SiO_2$ with 5 to 16.7% SnO_2 added to them showed that in this system the solubility of SnO_2 reaches of the order of 10% [2], and the glasses remain transparent. Glasses are opacified when the SnO_2 content is high. When 16.7% SnO_2 is added heat-treated glass manifests a high degree of opacity because of the limited solubility of SnO_2 and because of the additional precipitation of cassiterite crystals from melt during heat treatment.

The objective of additionally adding ZrO_2 was the need for increasing further both the chemical stability and the strength of the GCM.

Glasses with the following compositions (%) were studied: 50 SiO_2 , 12.5 K_2O , 12.5 Al_2O_3 , 8.3 Li_2O , and 16.7 SnO_2 into which 2, 4, 6, 8, and 10% ZrO_2 above 100% were added (glasses 1, 2, 3, 4, and 5, respectively).

The glasses were synthesized in porcelain crucibles in an electric furnace at temperature $1340 \pm 10^\circ C$ with soaking for 3 h at the final temperature. All initial glasses were characterized by a high degree of opacity.

X-ray phase analysis of the initial glasses (Fig. 1) showed that the opacification of these glasses is due to the presence of only a single crystal phase — cassiterite SnO_2 — not only precipitated from melt as it cools but also of relict

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² Here and below — content by weight.

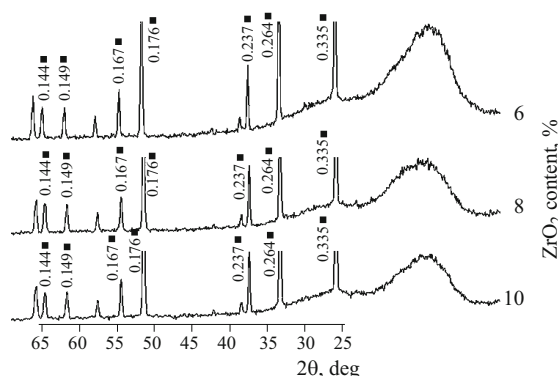


Fig. 1. X-ray diffraction patterns of the initial glasses No. 3 (6% ZrO_2), No. 4 (8% ZrO_2), and No. 5 (10% ZrO_2): ■) cassiterite.

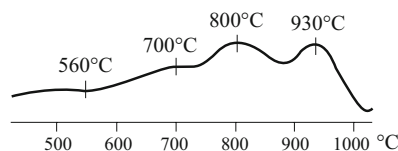


Fig. 2. DTA curve of glass No. 5 (8.3% Li_2O , 16.7% SnO_2 , and 10% ZrO_2).

origin in connection with its limited solubility in the silicate melt.

Zirconium oxide ZrO_2 completely passed into the glass phase. This suggests that the maximum amount of ZrO_2 capable of dissolving in the glasses of the experimental systems is somewhat higher than its solubility in low-alkali glasses of the system $\text{MgO} - \text{CaO} - \text{SiO}_2$ [8, 9], where it does not exceed 5 – 6%.

The increase of the ZrO_2 content is primarily due to the presence of a substantial amount of alkali-metal oxides (> 20%) in the experimental glasses, retarding the coordination transition of the zirconium oxides from the anionic part of the structure ($[\text{ZrO}_6]$ groups) into the cationic part ($[\text{ZrO}_8]$ groups).

The sequence of phase transitions during heat treatment is easily followed by means of DTA.

TABLE 1. Properties of Glass Crystalline Materials in the System $\text{K}_2\text{O} - \text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{SnO}_2 - \text{ZrO}_2$

Composition No.	Properties		
	CLTE, 10^{-6} K^{-1}	chemical solubility, %	bending strength, MPa
1	17.1	0.931	50.6
2	17.2	0.782	54.8
3	16.6	0.624	61.9
4	16.2	0.505	63.0
5	15.7	0.360	65.0

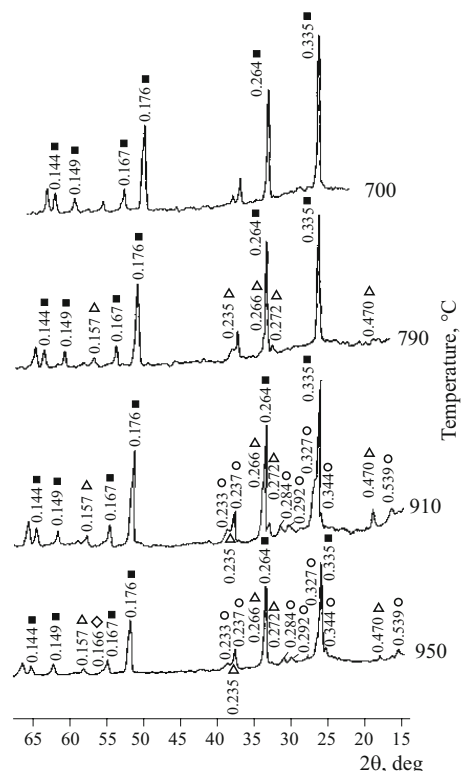


Fig. 3. X-ray diffraction pattern of glass No. 5 after heat-treatment: ■) cassiterite; ○) leucite; △) lithium metasilicate; ◇) baddeleyite.

The DTA curve for glass No. 5 with 10% ZrO_2 (Fig. 2) shows three exothermal effects. The first effect, which occurs at 700°C and is very weak, is due to additional release of SnO_2 from the melt, as a result of which for glass heat-treated at 700°C (Fig. 3) the cassiterite peaks are somewhat higher than for the initial non-heat-treated glass (see Fig. 1). Therefore the presence of relict cassiterite and the increase of its content as a result of its partial precipitation from the glass phase during heat treatment. According to the XPA data, heat treatment of glass at 800°C (second exo-effect) results in the appearance of a new phase — lithium metasilicate $\text{Li}_2\text{O} \cdot \text{SiO}_2$. Leucite only appears with heat treatment near the third exo-effect (910 – 950°C). The precipitation of baddeleyite in very small quantities is observed only with heat treatment above 950°C. The amount of baddeleyite is so small that the exo-effect associated with its precipitation does not appear on the DTA curve.

Thus, the most of the precipitated ZrO_2 remains in the glass phase even after heat treatment, having a strong effect on its chemical stability and mechanical strength.

According to Table 1, an increase of the ZrO_2 content from 2 to 10% in the presence of 16.7% SnO_2 results in a decrease of the chemical solubility from 0.931 to 0.360%. The values of the CLTE of crystallized samples also decrease in the presence of zirconium dioxide — from 17.1×10^{-6} to $15.7 \times 10^{-6} \text{ K}^{-1}$. The bending strength is the range 50 –

65 MPa, which corresponds to the requirements of the standard for the opaque layer of metal-ceramic dentures.

Thus, the phase composition formed for the glass crystalline material based on the system $K_2O - Li_2O - Al_2O_3 - SiO_2 - SnO_2 - ZrO_2$, first and foremost, leucite, cassiterite, and a glass phase, give the required properties (CLTE, chemical stability, mechanical strength) for obtaining an opaque layer of metal-ceramic dentures.

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